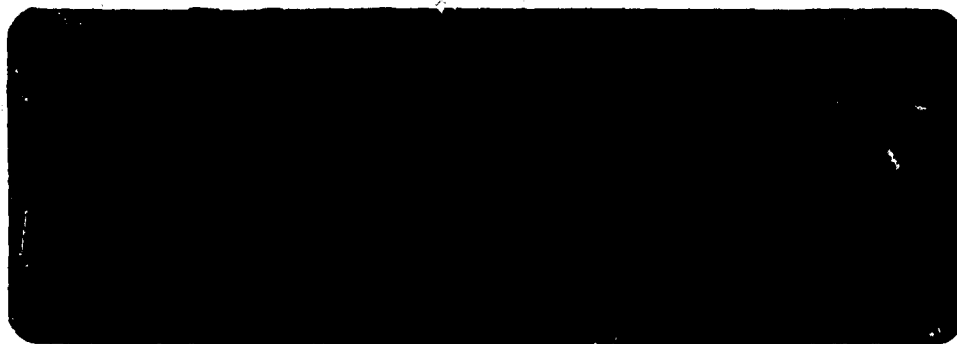


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SCIENTIFIC REPORT

ABSORPTION BY CO_2 BETWEEN 3100 AND 4100 cm^{-1}
(2.44 - 3.22 Microns)

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30 April 1968



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ABSTRACT

The absorption by CO_2 between 3100 and 4100 cm^{-1} has been studied with a spectrometer whose spectral slitwidth was approximately one-half cm^{-1} . Spectral curves were obtained for 26 samples of CO_2 and $\text{CO}_2 + \text{N}_2$ with pressures as high as 14.6 atmospheres and with paths as long as 933 meters. Several absorption bands not observed previously in laboratory spectra have been identified and the strengths of several bands have been determined. Absorption between 3770 and 4100 cm^{-1} by the extreme wings of strong lines at lower wavenumbers has been investigated for self-broadened and N_2 -broadened lines. Spectral curves and extensive tables of

$\int_{\nu'}^{\nu} A(\nu) d\nu$ have been included for most of the samples.

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SECTION 1

INTRODUCTION AND SUMMARY

Most of the absorption by CO_2 in the $3100\text{--}4100\text{ cm}^{-1}$ region is due to the 02^0_1 and 10^0_1 bands of $\text{C}^{12}\text{O}^{16}_2$ with centers at 3612.8 and 3714.3 cm^{-1} , respectively. However, many other difference bands, combination bands, and isotopic bands also occur in this spectral region. These CO_2 bands play a very important part in the emission by flames and rocket plumes and in the transfer of heat through the atmospheres of the earth and other planets.

Several quantitative measurements of the absorption in this region have been made previously with low resolution.^{1,2} The present investigation was undertaken to supplement the previous work with data on samples over wider ranges of pressure and absorber thickness and with sufficient resolution to resolve many of the individual lines. An absorption cell with paths as great as 933 meters has enabled us to study samples of very large absorber thickness without using such high pressures that the structure in the spectral curves would be smoothed out. Shorter absorption cells have also made it possible to study samples at pressures up to 15 atmospheres in order to measure the absorption coefficient and to determine band strengths accurately. Absorption in the $3770\text{--}4100\text{ cm}^{-1}$ region by the extreme wings of lines whose centers occur at lower wavenumbers has also been studied for pure CO_2 and for $\text{CO}_2 + \text{N}_2$ mixtures. The gas-handling procedures and the methods of recording and reducing the data have been described previously.^{3,4}

The data are presented in figures and tables of integrated absorptance, $\int A(\nu) d\nu$. Tables of transmittance versus wavenumber are available from the authors.

SECTION 2

SAMPLE PARAMETERS AND SPECTRAL CURVES

Table 2-1 contains the parameters of the samples investigated. Included in the table are the sample number; p , the partial pressure of CO_2 ; P , the total pressure due to CO_2 and N_2 ; L , the geometrical path length; and u , the absorber thickness, which is given by

$$u(\text{atm cm}_{\text{STP}}) = p(\text{atm}) [1 + 0.005p] L(\text{cm}) 273/296. \quad (2-1)$$

The quantity $273/296$ accounts for the difference in densities at standard temperature (273°K) and at room temperature (296°K) where all the measurements were made. $[1 + 0.005p]$ accounts for the non-linearity in the relationship between CO_2 pressure and density for the pressures used in the present study.

P_e , the equivalent pressure, was determined from the following equation:

$$P_e = Bp + p_{\text{N}_2} = (B-1)p + P, \quad (2-2)$$

where $B = 1.3$ is the self-broadening coefficient, the ratio of the self-broadening ability for CO_2 to the N_2 -broadening ability.¹

Figures 2-1 through 2-5 show spectral curves for all samples except 20, 21, 22, 23, and 25 which have been omitted since their pressures were high and the structure in the curves was smoothed out. The wavenumber scale in the figures changes slowly, but over small intervals it can be considered linear. The numbers enclosed in rectangles correspond to the sample numbers. The spectral slitwidth used to scan the curves varied as indicated in Table 2-2.

TABLE 2-1
SAMPLE PARAMETERS

Sample No.	p	P	P _e	p	P	P _e
	torr	torr	torr	atm	atm	atm
1	1,900	1,900	2,500	2.5	2.5	3.29
2	1,900	1,900	2,500	2.5	2.5	3.29
3	584	584	762	0.768	0.768	1.002
4	175	175	228	0.230	0.230	0.300
5	176	707	760	0.232	0.930	1.008
6	58.4	58.4	75.9	0.0768	0.0768	0.0999
7	17.5	71.0	76.3	0.023	0.0934	0.1003
8	335	660	761	0.441	0.868	1.002
9	5.8	5.8	7.54	0.00763	0.00763	0.00992
10	5.8	76.0	77.7	0.00763	0.100	0.102
11	335	660	761	0.441	0.868	1.002
12	1.75	7.1	7.62	0.0023	0.00934	0.0103
13	1.75	77	77.5	0.0023	0.101	0.102
14	33.5	752	762	0.0441	0.989	1.003
15	0.58	7.4	7.57	0.000763	0.00973	0.00996
16	33.5	752	762	0.0441	0.989	1.003
17	760	760	993	1.000	1.00	1.31
18	190	760	817	0.25	1.00	1.075
19	11,100	11,100	15,500	14.6	14.6	20.4
20	11,100	11,100	15,500	14.6	14.6	20.4
21	335	11,100	11,200	0.441	14.6	14.7
22	335	11,100	11,200	0.441	14.6	14.7
23	33.5	11,100	11,100	0.0441	14.6	14.6
24	11,100	11,100	15,500	14.6	14.6	20.4
25	2,775	11,100	11,200	3.65	14.6	15.8
26	643	11,100	11,300	0.846	14.6	14.9

TABLE 2-1 (Cont.)

SAMPLE PARAMETERS

Sample No.	L Path m	u atm cm STP	Pages on which spectra appear
1	933	218,000	2-8, 2-9, 2-12
2	237	55,000	2-8, 2-9, 2-12
3	237	16,900	2-8, 2-9, 2-12
4	237	5,040	2-9
5	237	5,070	2-9, 2-12
6	237	1,680	2-11
7	237	503	2-11
8	12.37	503	2-10
9	237	167	2-10
10	237	167	2-10
11	4.16	169	2-10
12	237	50.3	2-11
13	237	50.3	2-11
14	12.37	50.3	2-11
15	237	16.7	2-10
16	4.16	16.9	2-10
17	0.0132	1.22	2-10
18	0.0132	0.305	2-11
19	32.9	47,600	2-12
20	4.16	6,010	Not shown
21	12.4	505	Not shown
22	4.16	169	Not shown
23	12.4	50.4	Not shown
24	0.0134	19.4	2-11
25	0.0134	4.59	Not shown
26	0.0134	1.05	2-11

TABLE 2-2
SPECTRAL SLITWIDTHS

Wavenumber (cm^{-1})	Spectral Slitwidth (cm^{-1})
3100	0.45
3600	0.56
4000	0.67

In spite of considerable care which was exercised to remove the H_2O impurity from the CO_2 samples,^{3,4} there was still some structure in the original spectral curves due to H_2O absorption lines. This absorption was particularly troublesome between approximately 3740 cm^{-1} and 3900 cm^{-1} where the H_2O lines are strong and very large samples of CO_2 are required to produce significant absorption. In order to account for the H_2O absorption, spectral curves were obtained for samples of $\text{H}_2\text{O} + \text{N}_2$. The absorber thickness of H_2O was adjusted to approximately match that in the CO_2 sample, and the N_2 pressure was adjusted to match the half-widths of the lines. The matching was done by observing H_2O lines which are isolated from CO_2 lines. The original spectral curves were then corrected by comparing them with the $\text{H}_2\text{O} + \text{N}_2$ curves before they were replotted and digitized. In most cases, the corrections are probably sufficiently accurate that remaining errors in transmittance due to H_2O absorption are not more than a few percent.

The portion of the curve for Sample 6 above 3750 cm^{-1} was not scanned and, therefore, does not appear with the remainder of the curve in the middle panel of Fig. 2-4.

Table 2-3 contains a list of the CO_2 bands from which one might expect appreciable absorption in the $3100\text{--}4100\text{ cm}^{-1}$ region for the samples included in the present investigation. The first column of the table contains an arbitrary number assigned to each band. The position of the band center, the energy levels involved in the transition, and the isotopic species are given in the next three columns. The last column provides a reference to the source from which the information was obtained. SWP indicates that the band center was calculated from energy levels tabulated by Stull, Wyatt, and Plass.⁵ Positions of the other band centers were obtained directly from the sources indicated. The positions of the band centers are indicated in Figs. 2-1 to 2-5 by the band numbers listed in Table 2-3. The band numbers are not enclosed in rectangles.

TABLE 2-3

CO₂ BANDS

Band No.	Band Center -1 cm	Transition ^(a)	Isotope ^(b)	Authority ^(c)
1	3125.19	06 ⁰⁰ -01 ¹⁰	12, 16, 16	SWP
2	3154.65	06 ²⁰ -01 ¹⁰	12, 16, 16	SWP
3	3181.45	05 ¹⁰	12, 16, 16	PTB
4	3255.78	15 ¹⁰ -02 ⁰⁰	12, 16, 16	SWP
5	3274.87	14 ⁰⁰ -01 ¹⁰	12, 16, 16	SWP
6	3289.55	13 ¹⁰	13, 16, 16	SWP
7	3339.34	13 ¹⁰	12, 16, 16	PTB
8	3340.33	14 ²⁰ -01 ¹⁰	12, 16, 16	SWP
9	3396.64	22 ⁰⁰ -01 ¹⁰	12, 16, 16	SWP
10	3433.65	21 ¹⁰	13, 16, 16	SWP
11	3465.34	04 ⁰¹ -10 ⁰⁰	12, 16, 16	PTB
12	3473.675	04 ²¹ -02 ⁰⁰	13, 16, 16	C
13	3482.197	04 ⁰¹ -02 ⁰⁰	13, 16, 16	C
14	3490.349	02 ⁰¹	13, 16, 18	C
15	3497.6	30 ⁰⁰ -01 ¹⁰	13, 16, 16	C
16	3498.719	03 ¹¹ -01 ¹⁰	13, 16, 16	C
17	3500.54	21 ¹⁰	12, 16, 16	PTB
18	3517.300	12 ⁰¹ -10 ⁰⁰	13, 16, 16	C
19	3527.705	02 ⁰¹	13, 16, 16	C
20	3542.60	05 ¹¹ -03 ¹⁰	12, 16, 16	PTB
21	3552.824	04 ²¹ -02 ⁰⁰	12, 16, 16	C
22	3568.185	04 ⁰¹ -02 ⁰⁰	12, 16, 16	C
23	3571.105	10 ⁰¹	12, 16, 18	C
24	3580.295	03 ¹¹ -01 ¹⁰	12, 16, 16	C
25	3587.510	10 ⁰¹	13, 16, 18	C

TABLE 2-3 (Cont.)

CO₂ BANDS

Band No.	Band Center -1 cm	Transition (a)	Isotope (b)	Authority (c)
26	3589.609	12 ⁰ 1-10 ⁰ 0	12, 16, 16	C
27	3612.810	02 ⁰ 1	12, 16, 16	C
28	3621.264	20 ⁰ 1-10 ⁰ 0	13, 16, 16	C
29	3621.533	12 ⁰ 1-02 ⁰ 0	13, 16, 16	C
30	3632.876	10 ⁰ 1	13, 16, 16	C
31	3639.181	11 ¹ 1-01 ¹ 0	13, 16, 16	C
32	3641.530	12 ² 1-02 ² 0	13, 16, 16	C
33	3675.110	02 ⁰ 1	12, 16, 18	C
34	3692.396	12 ⁰ 1-02 ⁰ 0	12, 16, 16	C
35	3711.438	20 ⁰ 1-10 ⁰ 0	12, 16, 16	C
36	3714.757	10 ⁰ 1	12, 16, 16	C
37	3723.208	11 ¹ 1-01 ¹ 0	12, 16, 16	C
38	3726.610	12 ² 1-02 ² 0	12, 16, 16	C
39	3814.260	20 ⁰ 1-02 ⁰ 0	12, 16, 16	C
40	3856.72	14 ⁰ 0	12, 16, 18	SWP
41	3980.57	01 ¹ 2-02 ⁰ 0	12, 16, 16	SWP
42	4005.89	00 ⁰ 2-01 ¹ 0	12, 16, 16	B
43	4030.28	01 ¹ 2-02 ⁰ 0	12, 16, 16	SWP
44	3942.3	14 ⁰ 0 (PI)	12, 16, 16	SWP
45	4064.0	22 ⁰ 0 (PI)	12, 16, 16	SWP

(a) The lower energy level is 00⁰0 unless indicated otherwise.

(b) The numbers denote the isotopes of C, O, and O, respectively.

(c) Authority for position of band center. SWP, Stull, Wyatt, and Plass⁵; C, Courtoy⁶; PTB, Plyler, Tidwell, and Benedict⁷; and B, Benedict.⁸

(PI) denotes pressure-induced band.

Much of the absorption above 3770 cm^{-1} , particularly for samples at higher pressures, is due to the extreme wings of the strong lines whose centers occur at lower wavenumbers. This wing, or "continuum," absorption is discussed in Section 4. A few weak bands also contribute to the absorption in this region, as can be seen in Fig. 2-5. The relative contributions due to the wing absorption and the absorption by the weak bands can be determined by investigating samples at different pressures since the strengths of the weak bands are independent of pressure, while the absorption coefficient due to the wings of the lines is proportional to pressure.

There is a hint of a pressure-induced band near 4064 cm^{-1} , and possibly another near 3942 cm^{-1} , in the curves corresponding to Samples 1 and 19 in Fig. 2-5. The absorption coefficient for pressure-induced bands is also proportional to pressure; therefore, their contribution is difficult to distinguish from the wing absorption. However, the contour of the curve for Sample 19 suggests the presence of something besides the wing absorption near 4060 cm^{-1} . One would not expect the wing absorption to be nearly constant over a 30 cm^{-1} interval, as occurs between 4030 cm^{-1} and 4060 cm^{-1} , then suddenly decrease at higher wavenumbers. The R-branch of the $01^{12}-02^{00}$ band (No. 43) might contribute slightly between 4030 and 4060 cm^{-1} . However, the "extra" absorption seems to be as strong in the high-pressure samples as in the samples at lower pressure and larger absorber thickness. Therefore, some absorption by the 22^{00} (No. 45) pressure-induced band seems likely. Although absorption by the 14^{00} pressure-induced band (No. 44) centered at 3942.3 cm^{-1} cannot be confirmed, it probably makes a small contribution. Below approximately 3100 cm^{-1} , there is considerable absorption by the larger samples due to the relatively strong 01^{11} pressure-induced band centered at 3004 cm^{-1} .

After correcting for H_2O absorption, we were not able to account for some absorption near 3870 cm^{-1} which causes the deviation from a smooth contour in Fig. 2-5. The relative amounts of absorption at different pressures indicated that it was not due to wing absorption or to a pressure-induced band. However, Benedict⁸ has recently attributed absorption in this region in unpublished Venus spectra obtained with better resolution by Pierre and Janine Connes to the 14^{00} band (No. 40) of $\text{Cl}_2^{16}\text{O}^{18}$. According to Stull, Wyatt, and Plass,⁵ this band should be centered at 3856.72 cm^{-1} ; therefore, the R-branch is probably responsible for the "extra" absorption seen near 3870 cm^{-1} in Fig. 3-5. The P-branch is probably obscured by the rapidly changing wing absorption and the R-branch of the $20^{01}-02^{00}$ band (No. 39). Evidence of the other bands listed in Table 2-3 with SWP as the authority for the band center can be seen in Figs. 2-1 to 2-5. To the knowledge of the authors none of the bands denoted with SWP have been observed previously in the laboratory. However, all of these bands, as well as several even weaker ones, appear in the Venus spectra obtained by Connes and Connes.

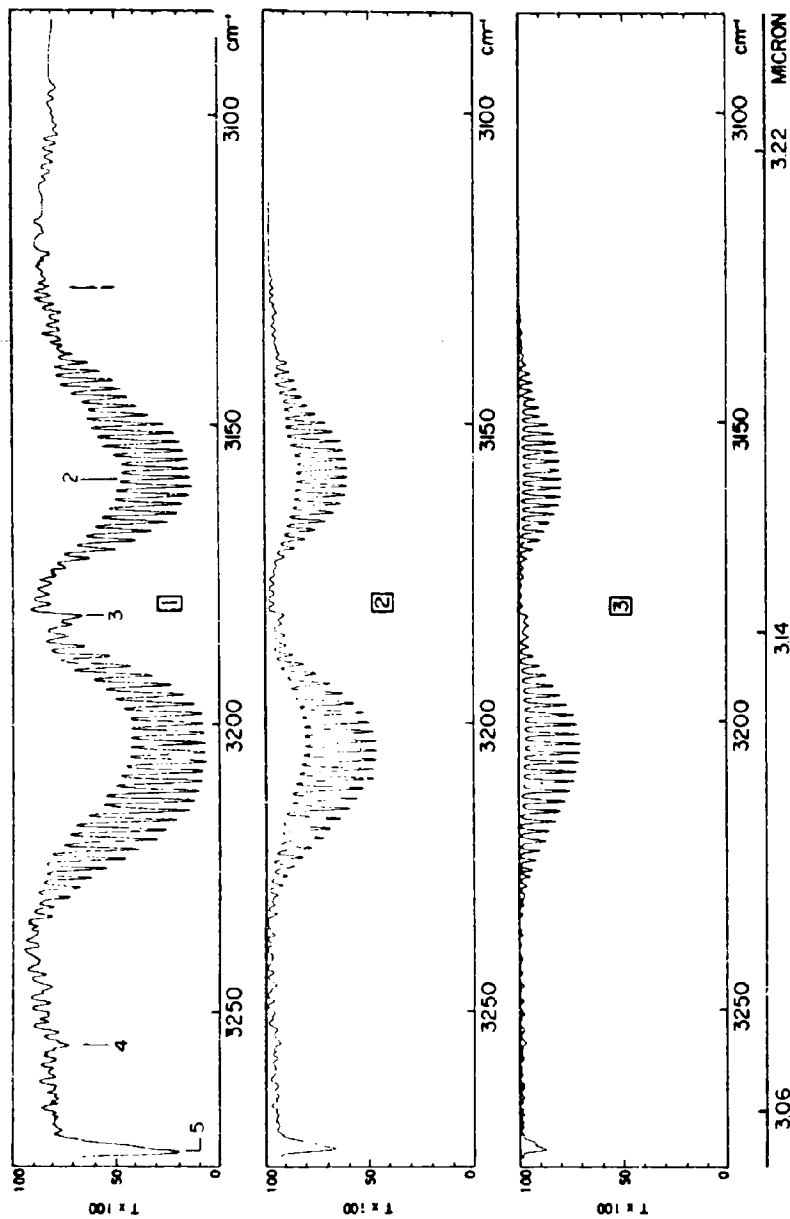


FIG. 2-1. CURVES OF TRANSMITTANCE VERSUS WAVENUMBER FOR VARIOUS SAMPLES.

The sample numbers are enclosed in rectangles. Positions of the band centers are indicated by the number which corresponds to the band number in Table 2-3. Figs. 2-2 through 2-5 are similar but for other spectral regions.

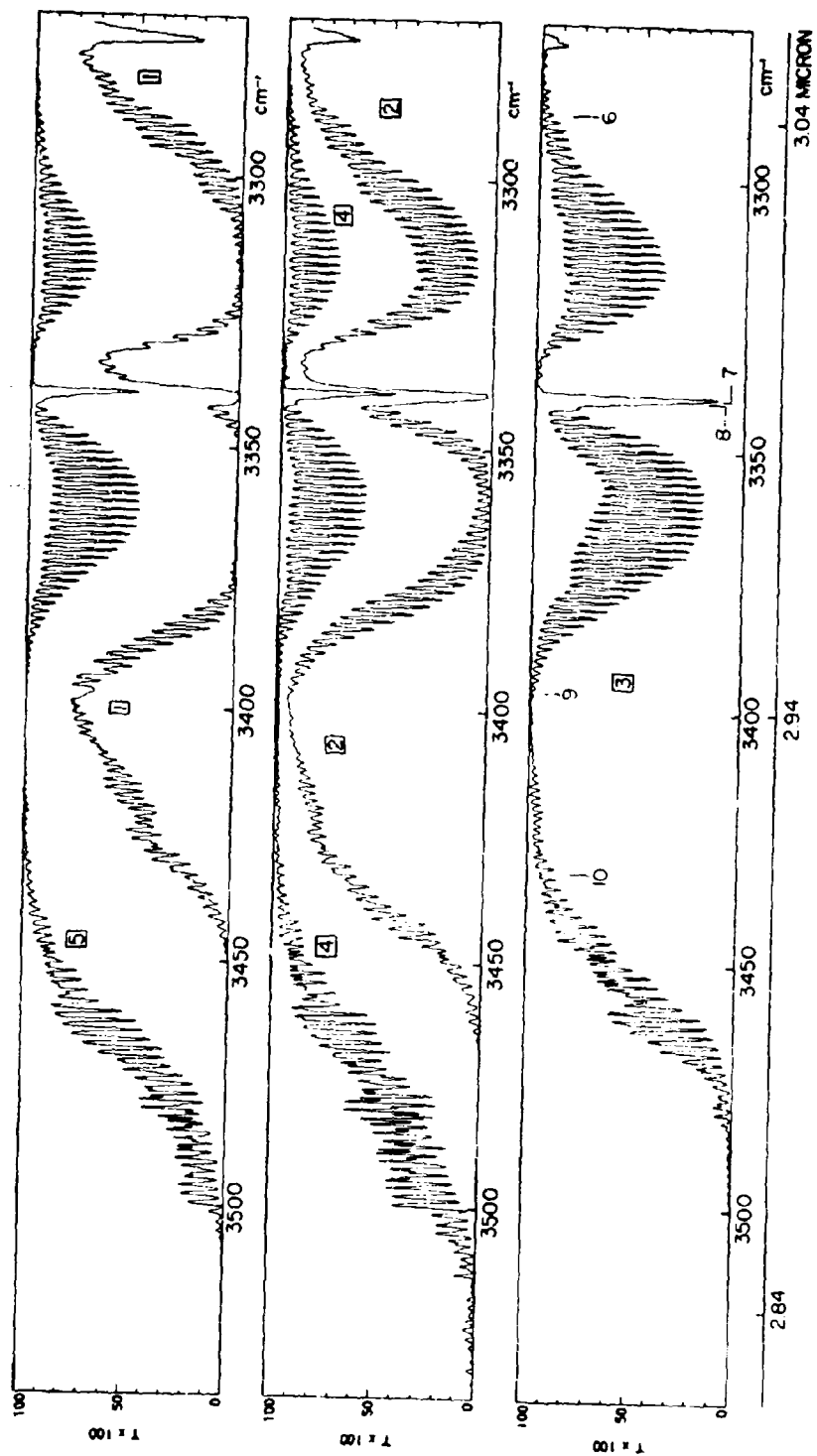


Fig. 2-2

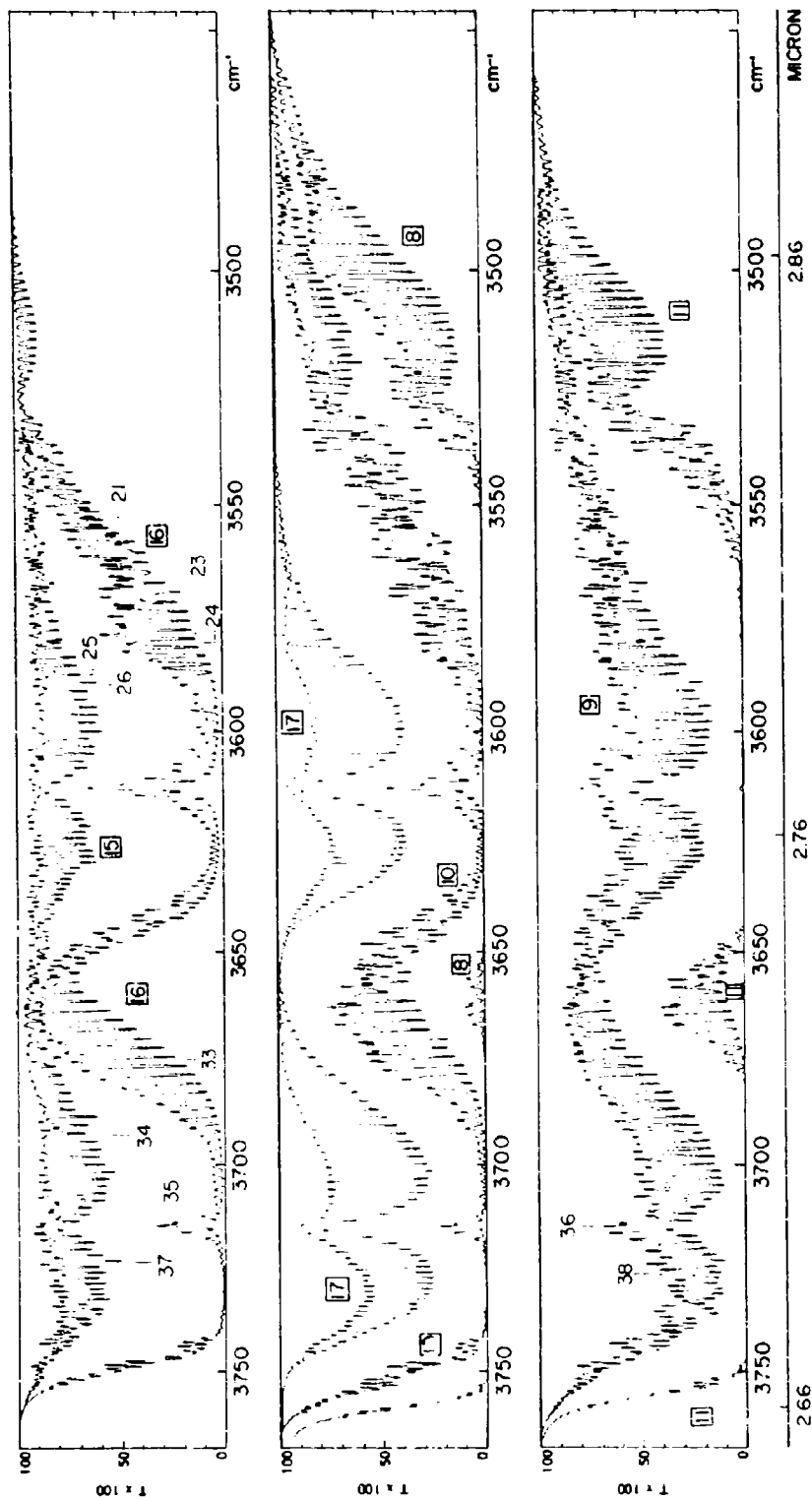


Fig. 2-3

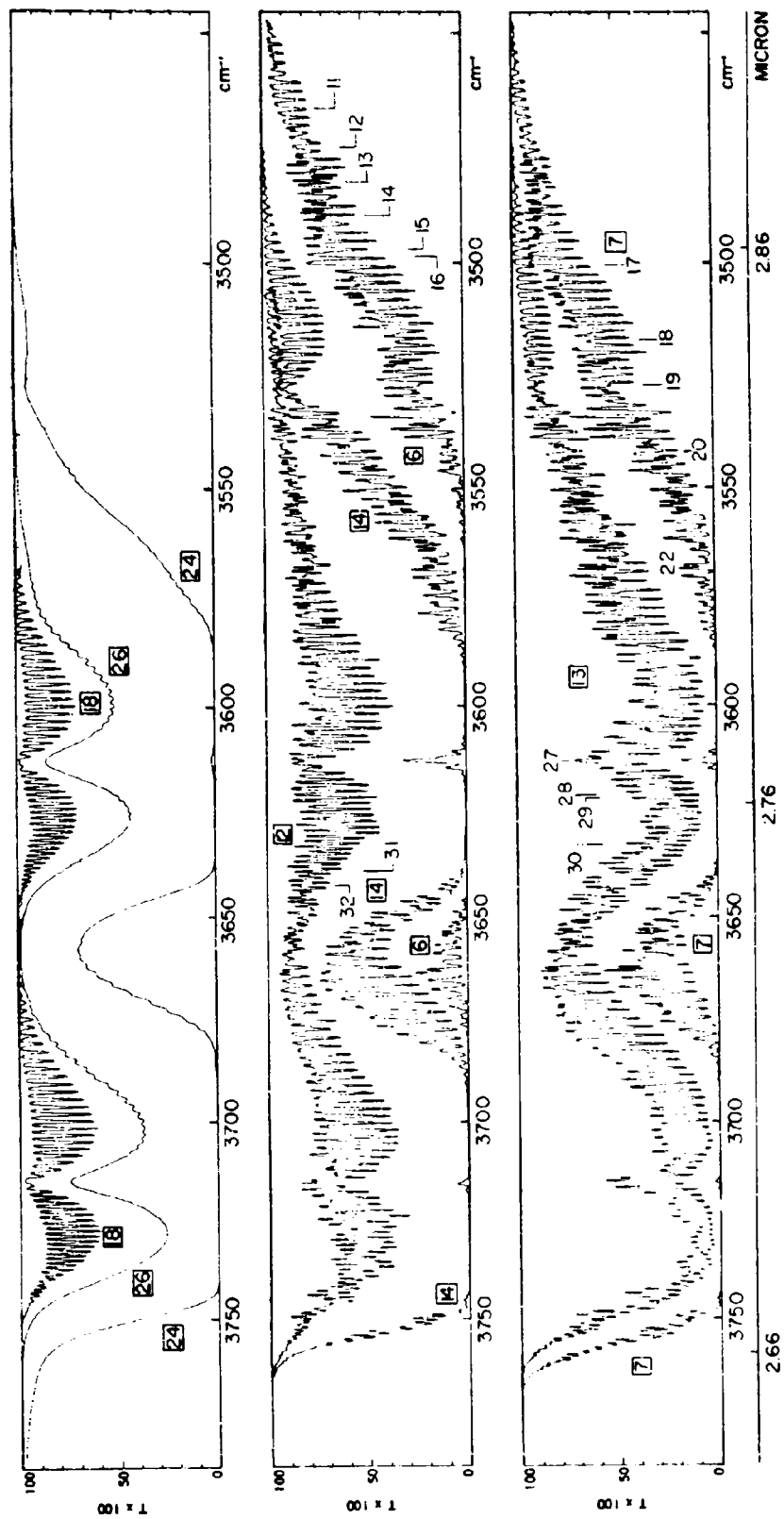


Fig. 2-4

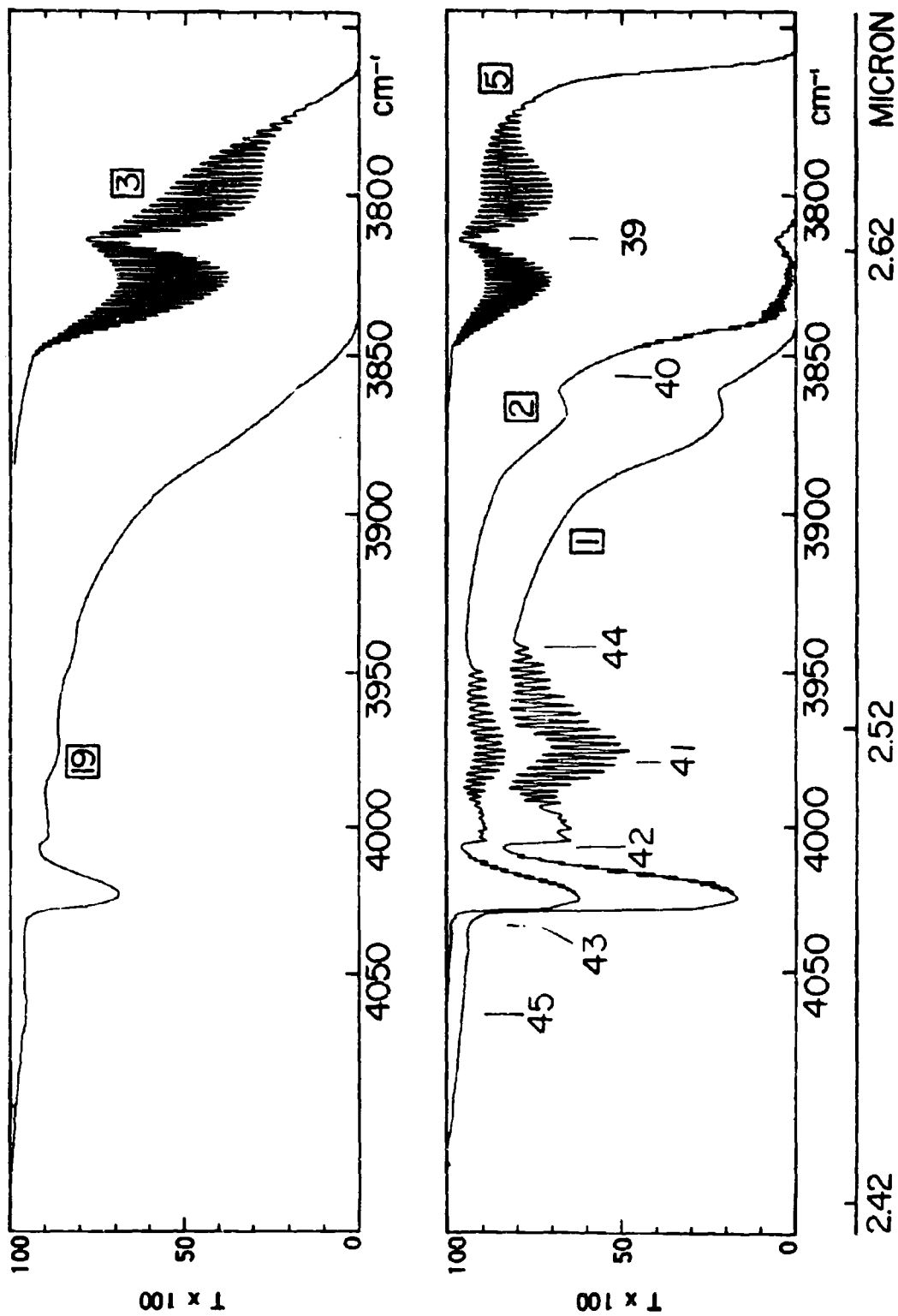


Fig. 2-5

SECTION 3

INTEGRATED ABSORPTANCE AND BAND STRENGTHS

Tables 3-1 to 3-3 give the integrated absorptance, $\int_{\nu'}^{\nu} A(\nu) d\nu$, for several of the samples investigated. ($A(\nu) \equiv 1-T(\nu)$) Each of the tables covers one of the three following spectral regions: 3090-3400 cm^{-1} , 3400-3764 cm^{-1} , and 3777.3-4100 cm^{-1} . Each column corresponds to the sample whose parameters are given at the top along with ν' , the lower limit of integration. In regions where the structure of the curves is regular, the cumulative integral is tabulated at points midway between the centers of the absorption lines. Therefore, if there is no overlapping, the difference between successive tabulated values is the integrated absorptance, or equivalent width, of the absorption line in the interval. In regions where there is little structure, or where it is irregular, the values are tabulated at convenient integral or half-integral wavenumbers. Tables of transmittance versus wavenumber have been compiled but are not included in this report because of their excessive size. However, copies can be obtained from the authors by workers who require them.

The 3400-3764 cm^{-1} region contains the strongest bands, and several of the larger samples are opaque ($A(\nu) = 1$) over wide intervals in this region. In some cases the integrated absorptance tables do not include the opaque regions, which are apparent in Figs. 2-1 to 2-5. The 3090-3400 and 3777.3-4100 cm^{-1} spectral regions contain weaker bands so that only the larger samples produce significant absorption. The intervals for which values have been tabulated for each sample are limited to places where the absorptance is sufficiently large to be measured with reasonable accuracy. In the interval between 3764 and 3777 cm^{-1} , which is not included in the tables, Samples 1, 2, and 19 are opaque. The absorptance in this interval changes rapidly with wavenumber for the smaller samples and is nearly negligible for Samples 9-18.

The cumulative integral, rather than the integral over short intervals, has been tabulated in Tables 3-1 to 3-3 in order that the integrated absorptance over any wavenumber interval listed in the tables can be found quickly by subtracting the values of the integral tabulated at the ends of the interval. The average absorptance over the interval is found by dividing the integrated absorptance by the width of the interval in cm^{-1} .

The true transmittance, $T'(v)$, that would be observed with infinite resolving power is related to the absorption coefficient $K(v)$ by

$$T'(v) = \exp [-uK(v)], \text{ or } K(v) = -\frac{1}{u} \ln T'(v). \quad (3-1)$$

We have shown in a previous report⁹ that if sample pressures are sufficiently high the line structure in a spectrum is smoothed out and $T(v)$, the observed transmittance, is approximately equal to $T'(v)$. Therefore, under this condition, the absorption coefficient can be determined from transmission spectra by substituting $T(v)$ for $T'(v)$ in Eq. (3-1). In the case of an isolated band which is not overlapped by a neighboring band, the strength S_v of the band is given by

$$S_v = \int K(v) dv = -\frac{1}{u} \int \ln T'(v) dv. \quad (\text{non-overlapping band}) \quad (3-2)$$

When there is overlapping of two or more bands, the contributions of each to the absorption must be determined before their strengths can be found.

By investigating samples covering very wide ranges of absorber thickness and at pressures up to 14.6 atm, we have determined $-\frac{1}{u} \int \ln T'(v) dv$ over six spectral regions from 3120 to 3780 cm^{-1} . As can be seen below, these six regions were chosen over intervals which are convenient for determining the strengths of the different branches of several bands. The results are summarized in Table 3-4 which also lists the bands contributing to the absorption in each of the spectral regions. Although relatively high pressures were required to measure $-\frac{1}{u} \int \ln T'(v) dv$, it should be noted that this quantity is essentially independent of pressure over the regions listed in Table 3-4 if P is less than 4 or 5 atm. However, as mentioned in the previous section, the absorption coefficient on either side of the interval covered in the table increases with pressure, because of the pressure-induced bands and the wing absorption.

Table 3-1 $\int_1^{\infty} A(\nu) d\nu$ [illegible]

Table 3-1 $\int A(\nu) d\nu$ (cont'd)[illegible]

[The page contains extremely faint, illegible markings that appear to be bleed-through or artifacts from another document.]

Table 3-2 $\int_2^{\infty} \bar{A}(v) dv$ (cont'd)[illegible]

Table 3-2 $\int_2^{\infty} A(\nu) d\nu$ (cont'd)[illegible]

$$\int_{\gamma} A(z) dz$$
[illegible]

TABLE 3-4
INTEGRATED ABSORPTION COEFFICIENT

Spectral Region (cm^{-1})	$-\frac{1}{u} \int L_n T'(\nu) d\nu$ ($\text{atm}^{-1} \text{cm}^{-1} \text{STP} \text{cm}^{-1}$)	Contributing Bands
3120.0 - 3249.0	3.8×10^{-4}	1, 2, 3
3249.0 - 3280.0	4.4×10^{-5}	4, 5, 6
3280.0 - 3400.0	3.2×10^{-3}	6 - 9
3400.0 - 3470.0	3.3×10^{-3}	9 - 13
3470.0 - 3658.3	32.4	12 - 32
3658.3 - 3780.0	47.7	32 - 38

The major sources of error in measurements of $(-1/u) \int L_n T'(\nu) d\nu$ are:

- (i) errors in sampling which produce errors in the value of u ,
- (ii) errors caused by differences between $T'(\nu)$ and $T(\nu)$ which arise because the lines are not sufficiently broadened, or the spectral slitwidth is too great, and
- (iii) errors in placing the zero-absorptance curve on the sample curve.

Errors due to (i) are probably less than one percent when pure CO_2 samples are used. However, this type of error may be as large as 2 or 3 percent in Samples 25 and 26, which were used from approximately 3570 to 3640 cm^{-1} and from 3675 to 3750 cm^{-1} . The additional uncertainty in these samples arises from pre-mixing the CO_2 and N_2 before introducing the mixture into the 1.34 cm cell. Errors due to (ii) are usually less than 1 or 2 percent if the samples are at approximately 14.6 atm and the transmittance is not too low. We⁹ have discussed previously the dependence of this type of error on line width, line spacing, and transmittance. In order to minimize this type of error, we restricted the samples used in a given spectral region to those whose transmittances were greater than approximately 0.2.

Errors of type (iii) are probably the most serious, particularly in regions where the absorptance is small. Wherever possible, we used samples only in regions where the absorptance was greater than approximately 0.2 in order to minimize this error. This was not possible in the narrow regions of weak absorption near 3120 cm^{-1} and 3250 cm^{-1} where even the largest 14.6 atm sample (19) produced less than 0.2 absorptance. The total estimated uncertainties for the values in Table 3-4 are $\pm 8\%$ for the $3120.0\text{--}3249.0\text{ cm}^{-1}$ region and $\pm 5\%$ for the other regions.

The value $32.4 \pm 5\% \text{ atm}^{-1} \text{ cm}^{-1}$ for the $3470\text{--}3658.3\text{ cm}^{-1}$ region, agrees favorably with $37 \pm 20\% \text{ STP}$ obtained by Burch, Gryvnak, and Williams¹ and $27.3 \pm 10\%$ by Eggers and Crawford.¹⁰ The latter two values were obtained with instruments having considerably lower resolving power and with samples at lower pressures so that the required corrections for the effect of the finite slit width were greater. Therefore, the present value is regarded as more reliable. The same comments apply to a similar comparison of the $47.7 \pm 5\% \text{ atm}^{-1} \text{ cm}^{-1}$ obtained for the $3658.3\text{--}3780.0\text{ cm}^{-1}$ region. Burch, Gryvnak, and Williams¹ reported $54 \pm 20\%$, while Eggers and Crawford¹⁰ obtained $39.1 \pm 10\%$ in the same units.

Although several bands contribute to the absorption in each of the optical regions listed in Table 3-4, four of the six regions contain one band which gives rise to most of the absorption. By following the procedure described previously¹¹ to account for the overlapping bands, difference bands, and isotopic bands, we have been able to determine the strengths of each branch of the major bands (3, 7, 27, and 36) in these four regions. The strength, S_Q , of the prominent Q branch of Band No. 5 was also determined, although overlapping by lines of other bands made it impractical to attempt to determine the strengths of the P and R branches. The strengths of these bands are given in Table 3-5 along with the strengths of Bands 39 and 42 (S_v denotes the strength of an entire band). The uncertainties in the strengths of Bands 3, 7, 27, and 36 are only slightly greater than the uncertainties in the corresponding values of integrated absorption coefficient listed in Table 3-4 since the corrections made for overlapping bands are relatively small. Overlapping by the continuum due to the wings of the strong lines at lower wavenumbers also had to be accounted for in order to determine the strengths of Bands 39 and 42. Since the continuum was quite significant at high pressures, the strengths could not be determined as accurately as for the other bands listed in Table 3-5.

Plyler, Tidwell, and Benedict⁷ have measured the strengths of Bands 3 and 7 and have determined from lines P72-74 the strength of Band 27. We have modified their results to account for the difference between the density of CO_2 at 273°K and at 298°K , and the temperature of their samples, so that we can compare them with our values given in $\text{atm}^{-1} \text{ cm}^{-1}$ STP cm^{-1} . These results are also given in Table 3-5. Although Plyler et al have

stated that their techniques were not designed to yield strength measurements of high precision, their results are in fair-to-good agreement with ours. The principal uncertainty in the measurements of Plyler et al arose from the presence of atmospheric H_2O lines and from the noise level. These sources of errors were greatly reduced in the present investigation since the optical path outside the absorption cell was evacuated and the larger sample produced absorption which was much greater than the noise. Abnormalities in the distribution of the strengths within the P, Q, and R branches of several bands in this spectral region have been discussed by Plyler et al.

TABLE 3-5
BAND STRENGTHS (T = 296°K)

Band No.	Band Center (cm ⁻¹)	Transition	Strengths (atm ⁻¹ cm ⁻¹ STPcm ⁻¹)	
			Present Results	Plyler et al*
3	3181.45	05 ¹ 0	S_P $1.1 \times 10^{-4} \pm 10\%$ S_{R+Q} $2.4 \times 10^{-4} \pm 8\%$ S_V $3.5 \times 10^{-4} \pm 8\%$	$3.6 \times 10^{-4} \pm 10\%$
5	3274.87	14 ⁰ 0-01 ¹ 0	S_Q $1.9 \times 10^{-5} \pm 20\%$	
7	3339.34	13 ¹ 0	S_P $7.0 \times 10^{-4} \pm 6\%$ S_Q $2.1 \times 10^{-4} \pm 10\%$ S_R $2.0 \times 10^{-3} \pm 6\%$ S_V $2.9 \times 10^{-3} \pm 6\%$	$3.8 \times 10^{-4} \pm 10\%$
27	3612.81	02 ⁰ 1	S_P 13.8 $\pm 6\%$ S_R 15.2 $\pm 6\%$ S_V 29.0 $\pm 6\%$	33 $\pm 10\%$
36	3714.76	10 ⁰ 1	S_P 21.3 $\pm 6\%$ S_R 23.6 $\pm 6\%$ S_V 44.9 $\pm 6\%$	
39	3814.26	20 ⁰ 1-02 ⁰ 0	S_P $9.1 \times 10^{-4} \pm 20\%$ S_R $10.5 \times 10^{-4} \pm 20\%$ S_V $19.6 \times 10^{-4} \pm 20\%$	
42	4005.89	00 ⁰ 2-01 ¹ 0	S_{P+Q} $5.4 \times 10^{-5} \pm 15\% - 5\%$ S_R $9.5 \times 10^{-5} \pm 10\% - 2\%$ S_V $14.9 \times 10^{-5} \pm 12\% - 3\%$	

*Plyler, Tidwell, and Benedict⁷

SECTION 4

WING ABSORPTION BETWEEN 3780 AND 4100 cm^{-1}

The contribution to the absorption between 3780 and 4100 cm^{-1} by the lines occurring in the region can be estimated and subtracted from the observed absorption to obtain the contribution by the extreme wings of the strong lines whose centers occur at lower wavenumbers. The following discussion refers only to the absorption by the extreme wings, which is frequently called continuum absorption because of the lack of structure in the spectrum.

It is well known that the absorption coefficient of a single, collision-broadened absorption line is proportional to pressure at any point more than a few half-widths from the line center. Therefore, since the continuum absorption between 3780 and 4100 cm^{-1} is due to the sum of the wing contributions of many lines, we expect the absorption coefficient to be proportional to pressure. We¹² have previously demonstrated this to be true for continuum absorption above the head of the 1.4 μ (00⁰3) CO_2 band.

For a sample of pure CO_2 , when there is self-broadening only, the absorption coefficient is given by

$$K_s(\nu) = K_s^0(\nu)p/p^0, \quad (4-1)$$

where the subscript s refers to self-broadening and the superscript o indicates a pressure of 1 atm. Since there is no structure in the continuum absorption and it does not change appreciably over an interval equal to our spectral slitwidth, we assumed that the observed transmittance was equal to the true transmittance $T(\nu)$. Therefore, we were able to determine the absorption coefficient for the continuum from the spectral

curves, after accounting for the nearby lines, by the use of Eq. (3-2). By combining this equation with Eq. (4-1), we get for a pure CO₂ sample,

$$K_s^0(\nu) = \frac{p^0}{p_{up}} L T(\nu). \quad (4-2)$$

In the case of a mixture of CO₂ plus a non-absorbing foreign gas with partial pressure p_f , the absorption coefficient results from the sum of the self-broadening and the foreign-broadening and is given by

$$K(\nu) = K_s(\nu) + K_f(\nu). \quad (4-3)$$

Since K_f is proportional to p_f , we can write

$$-\frac{1}{L} \ln T(\nu) = K_s^0(\nu) p/p^0 + K_f^0(\nu) p_f/p^0. \quad (4-4)$$

From curves of transmittance for pure samples covering wide ranges of pressure and path length, we have determined $K_s^0(\nu)$ at several points where the contribution by nearby lines is small. The results are shown in Fig. 4-1, along with similar results for N₂ broadening. The latter results were obtained from curves for CO₂ + N₂ mixtures by the use of Eq. (4-4) after K_s^0 had been determined. Most of the points are based on samples at pressures from approximately 7 to 15 atm, since the relative contribution of the nearby lines is less at high pressures. The greatest uncertainty in the results is due to errors in accounting for the nearby lines. The estimated uncertainty in the curves of Fig. 4-1 is approximately $\pm 10\%$ for $\nu < 3900 \text{ cm}^{-1}$; at higher wavenumbers, it increases to approximately $\pm 30\%$ at 4100 cm^{-1} .

It is of interest to note that $K_{N_2}^0$ is only about 0.1 times as great as K_s^0 near 3780 cm^{-1} , but it is nearly $^{12} 0.5$ times as great near 3900 cm^{-1} . We¹³ have shown previously that the absorption coefficient at about 1 cm^{-1} from the center of an N₂-broadened line is approximately 0.8 times as great as that for an equally-strong, self-broadened line when the pressures are equal. Therefore, since $K_{N_2}^0/K_s^0$ is as small as 0.1 at a point where most of the absorption is due ² to distant lines, we can conclude that the shapes of the wings of self-broadened and N₂-broadened lines are quite different. A separate report¹⁴ dealing with the shapes of the wings of lines in this region and in the 1.4 and 4.3 μ regions is being written.

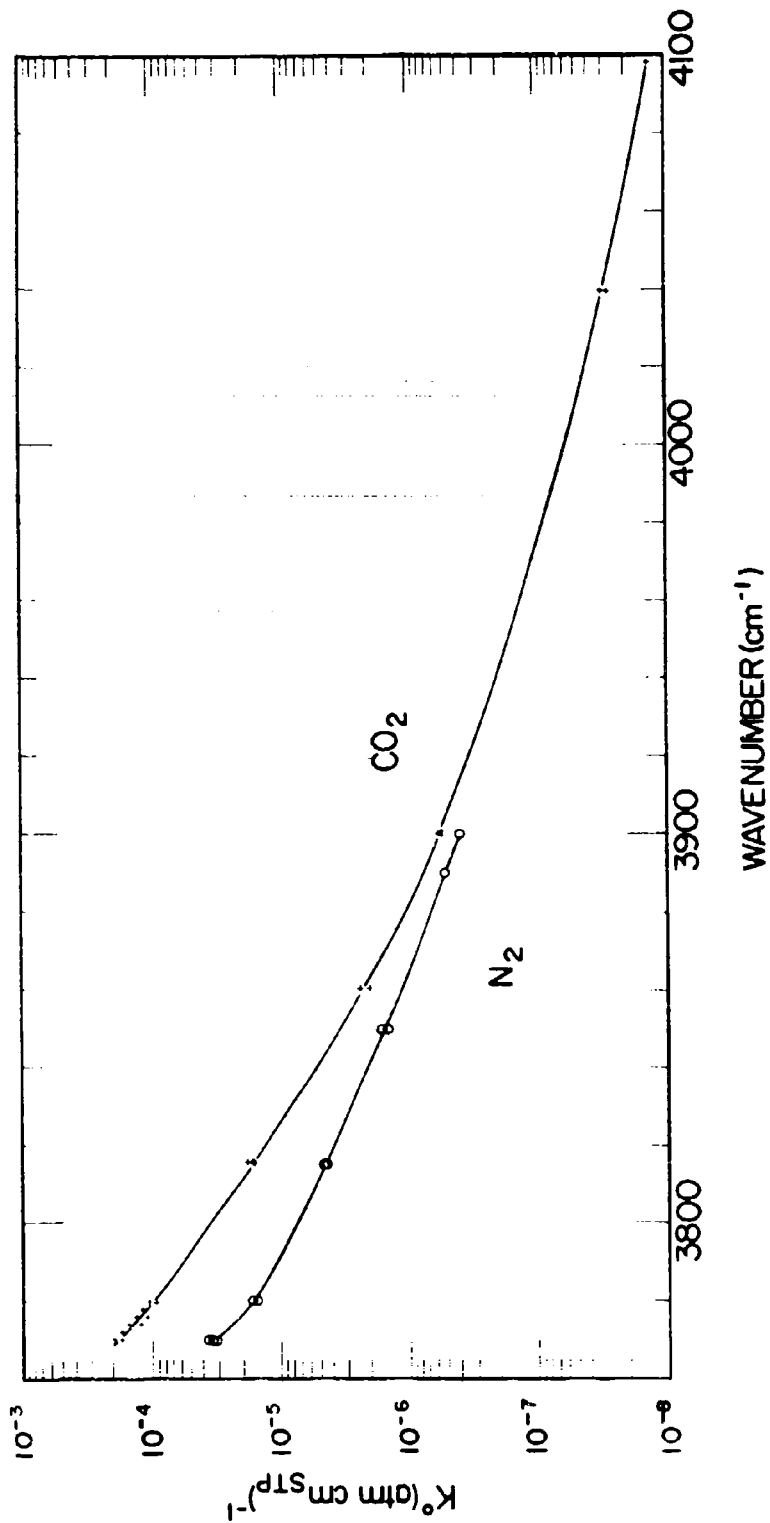


FIG. 4-1. ABSORPTION COEFFICIENT BETWEEN 3770 AND 4100 cm^{-1} DUE TO WINGS OF STRONG CO_2 LINES AT LOWER WAVENUMBERS.

The upper curve corresponds to self-broadening and the lower curve to N_2 broadening at 1 atm pressure.

SECTION 5

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13 ABSTRACT <p>The absorption by CO₂ between 3100 and 4100 cm⁻¹ has been studied with a spectrometer whose spectral slitwidth was approximately one-half cm⁻¹. Spectral curves were obtained for 26 samples of CO₂ and CO₂ + N₂ with pressures as high as 14.6 atmospheres and with paths as long as 933 meters. Several absorption bands not observed previously in laboratory spectra have been identified and the strengths of several bands have been determined. Absorption between 3770 and 4100 cm⁻¹ by the extreme wings of strong lines at lower wavenumbers has been investigated for self-broadened and N₂-broadened lines. Spectral curves and extensive tables of $\int^v A(v)dv$ have been included for most of the samples.</p>			

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14 KEY WORDS CO ₂ Infrared Absorption Collision Broadening Line Shapes Band Strengths	LINK A		LINK B		LINK C	
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